"EFFECT OF ELECTROLYTE SOLUTIONS ON SUNFLOWER OIL WATER INTERFACIAL TENSION IN PRESENCE OF SURFACTANTS"

Thesis Submitted by

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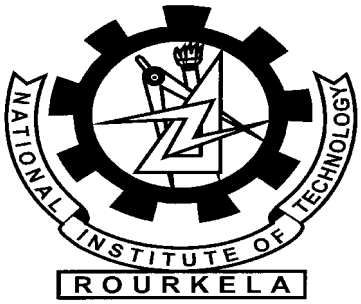
In partial fulfilment for the award of the Degree of

Master of Technology (Chemical Engineering)

Under the Guidance of

Dr. Santanu Paria



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May 2014

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CERTIFICATE

This is to certify that the project report entitled, "**Effect of electrolyte solutions on sunflower oil water interfacial tension in presence of surfactant**" submitted by Meghna Sheoran in partial fulfilment for the requirements for the award of Master of Technology Degree in Chemical Engineering at National Institute of Technology, Rourkela (Deemed University) is an authentic work carried out by her under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University / Institute for the award of any Degree or Diploma.

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ACKNOWLEDGEMENT

I would like to make my deepest appreciation and gratitude to Dr. Santanu Paria for his invaluable guidance, constructive criticism and encouragement during the course of this project.

Grateful acknowledgement is made to all the staff and faculty members of Chemical Engineering Department, National Institute of Technology, Rourkela for their encouragement. I want to acknowledge the support and encouragement of Mr. K. Jagajjanani Rao and Mr.Siddhartha Sankar Boxi in the lab work. I am also thankful to Miss Khushi Mukherjee, Miss Aritri Ghosh and Mr Rahul Purbia for making and maintaining a lively atmosphere in the lab.

I thank my parents and family members for the support, encouragement and good wishes, without which it would have been difficult to complete my thesis. I would also like to extend my sincere thanks to all my fellow students for their time, invaluable suggestions and help.

Date: May 5, 2014

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ABSTRACT

The basic ingredients of cosmetics are usually an oil phase, water phase and a surfactant. Anionic surfactants are usually used in cosmetics as they have lower CMC values. But due to presence of an oily phase the surfactant used should have antifungal or antibacterial properties also. So CTAB was used as surfactant due to its antifungal properties and ability to withstand precipitation in presence of electrolytes. Interfacial tension is an important property for characterization of microemulsions. This report mainly focuses on the effect of inorganic electrolytes on interfacial tension in the sunflower oil/water system in the presence of a cationic surfactant. The objective of this study is to obtain insight into the effect of different electrolytes such as sodium chloride, calcium chloride, sodium phosphate and sodium sulphate on the surfactant adsorption characteristics. The experimental interfacial isotherms were fitted with Langmuir and Frumkin Adsorption models. The results indicate an increase in surfactant adsorption in presence of electrolytes. Also higher concentration of electrolyte increases the surfactant adsorption by screening electrostatic repulsions between surfactant head groups.

Keywords: Cationic surfactant, Interfacial tension, Du Nuoy ring tensiometry, Electrolyte, Langmuir adsorption isotherm, Frumkin adsorption Isotherm.

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NOMENCLATURE

CMC	Critical Micellar Concentration
CTAB	Cetyltrimethylammonium bromide
XRD	X-ray diffraction
NaCl	Sodium Chloride
$CaCl_2$	Calcium Chloride
Na_3PO_4	Sodium Phosphate
Na_2SO_4	Sodium Sulphate
DLS	Dynamic light scattering
IFT	Interfacial tension
BET	Brunauer Emmett Teller
GDS	Gibbs dividing surface
T	Temperature
P	Pressure
UV	Ultraviolet
DIT	Dynamic interfacial tension
SEM	Scanning electron microscope

LIST OF SYMBOLS

	Surface excess concentration
C	Concentration of surfactant in liquid phase at adsorption equilibrium
b	Adsorption equilibrium constant
ω	Area covered by one molecule in surface layer
G	Gibbs free energy
A	Interfacial area
ɵ	Surface coverage
ϵ	Compressiblity coefficient
€	Error in fitting
R	Universal gas constant
a	Frumkin interaction costant
c_2	Concentration of salt
∏	Surface pressure
γ	Interfacial tension
I	Ionic strength
f	Activity coefficient of solution

CHAPTER 1

INTRODUCTION

An oily phase, an aqueous phase and a surfactant sometimes along with co-surfactant are basically the ingredients of a microemulsion. The micreostructure of microemulsions depends on the ratio of the components. They may contain little water droplets dispersed in oil phase or oil droplets dispersed in water phase. The microemulsions of each kind are thermodynamically stable. They have a variety of applications such as detergency, drug delivery, catalysis, enhanced oil recovery, nanoscale particle production, flammability control, etc.

According to Flanagan et al. [1], microemulsion characterization can be divided into two main areas, i.e. characterization at the microscopic and macroscopic levels. The interfacial tension represent the macroscopic level measurements. For a fine emulsion it is important for solubilisation to be large and interfacial tension to be very low. In other words, interfacial tension is an important property.

1.1 Interfacial Tension:

An interface is boundary between any two immiscible phases whereas if one phase is gas then the interface is called a surface. It is shown in figure 1.1. There are five different interfaces viz. i) Solid-vapor, ii) Solid-liquid, iii) Solid-solid, iv) Liquid-vapor, v) Liquid-liquid. Interfacial tension is basically the force that prevents molecules of one fluid from invading the other.

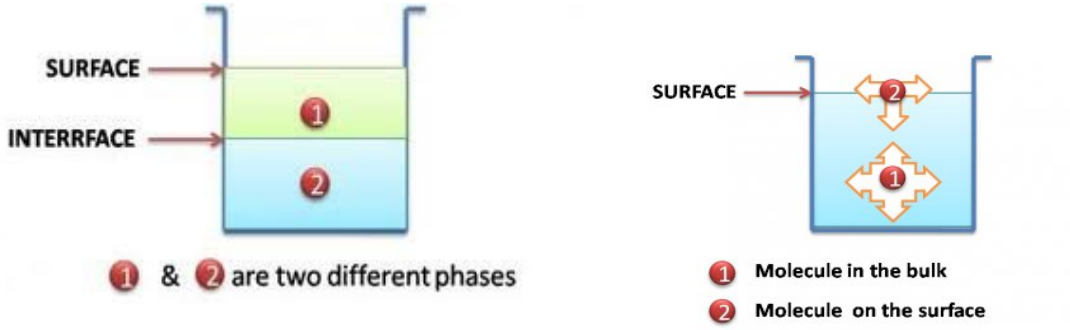


Figure 1.1 Schematics of Interfacial Tension

As shown in the figure, molecules in the bulk phases are surrounded by similar molecules and therefore have net force of zero acting on them. On the other hand, when the molecule comes to the interface they are forced to come to molecules of the other bulk phase and therefore a net force acts on them. So interfacial tension is the amount of work that should be supplied to bring the molecules from the bulk phases to the contact boundary to create a new interface of unit area. As a result of this, energy is minimized and the surface tends to contract so surface energy can also be expressed as a tension force per length. The amount of energy required to create a surface per unit area is called the surface free energy and can be related to Gibbs free energy as follows:

$$dG = \gamma dA(\text{At constant } T, P)$$

where, dG=Gibbs Free Energy and γ=Surface Free Energy.

The interfacial tension can further be related to adsorption isotherms. An adsorption isotherm is a graph between the concentration of adsorbate at the interface and the concentration in the bulk. A number of adsorption isotherms are there such as Langmuir Adsorption Isotherm, Freundlich Isotherm, BET Isotherm,etc. Each has different assumptions and used in different conditions. For liuid-liquid interface, Frumkin model has been found to give the best fit as it takes into consideration additional lateral interactions between adsorbed surfactant molecules at interface.

1.2 Importance of surfactants:

Surfactants are polar organic compounds which contain a hydrophilic part and a hydrophobic part. They are amphiphilic in nature which makes them suitable for a variety of applications. When they are added to an oil-water mixture interfacial tension is lowered. A large number of industrial processes such as enhanced oil recovery (Gracia et al. [2]), microemulsion formation, etc. require a basic understanding of the interfacial tension. The significance of surfactants has also increased numerous folds in food, cosmetic and pharmaceutical industry. Based on the nature of their hydrophilic part they are classified as:

Table 1.1 Classification of Surfactant**s**

Sr. No.	**Type of Surfactant**	**Description**	**Examples**
1	Anionic Surfactant	Hydrophilic group carries a negative charge	RC6H4SO3 $^{-}Na^{+}$ (alkyl benzene sulphonates)
2	Cationic Surfactant	Hydrophilic group carries a positive charge	quaternary ammonium halides ($R_4N^{+}Cl^{-}$)
3	Amphoteric or Zwitter-ionic Surfactants	Molecules can potentially contain both a positive and negative charge	long chain amino acids $RN^{+}H2CH2\text{-}COO^{-}$
4	Non-ionic Surfactant	Hydrophile bears no charge	RCOOCH2CHOHCH2OH (monoglyceride of long chain fatty acid)

1.3 Properties of Sunflower oil:

Sunflower oil is mainly a triglyceride. Its smoke point is 232^{o} C and density is 0.9188 g/cm^{3}. Its composition is:

i) Palmitic Acid (saturated) 4-9%

ii) Stearic Acid (saturated) 1-7%

iii) Oleic Acid (monounsaturated omega) 14-40%

iv) Linoleic Acid (polyunsaturated omega) 48-74%

It is used in food industry due to its useful properties. The triglycerides present in it act as natural surfactants

1.4 Effect of surfactants on interfacial tension:

Interfacial phenomena is significant in various applications such as emulsions, pharmacy, medicine, etc. It is the interfacial phenomena only that affects adsorption of drugs onto solid adjuncts in dosage forms. However surfactants have potential to alter this interfacial phenomena. It is the hydrophilic and hydrophobic nature of surfactants that induce a large number of properties in surfactants including micelle formation. When surfactants are added to a liquid, the surface tension and if to an oil water interface, the interfacial tension goes on decreasing with the concentration of surfactant till CMC where micelle formation takes place. During this process, surfactant molecules will adsorb at the interface in such a manner that the overall free energy of the system is lowered.

Both non-ionic and ionic surfactants alter the interfacial tension. However, due to properties of counterion binding and surface electric potential ionic surfactants are more effective in altering the interfacial tension. Cationic surfactants have very low CMC and can be used even in hard water. They found increased importance after their bacteriostatic properties were recognised for the first time in 1935 by Domagk.

1.5 Effect of salts on interfacial tension:

Salts such as sodium chloride, calcium chloride and sodium phosphate are being used in food and cosmetic industry due to one purpose or other. Sodium chloride is used as flavour enhancer, intensifier, dough conditioner, oral care agent, flavoring agent, viscosity increasing agent, and is also seen as a thickener in some cases, as an abrasive in scrub products; calcium chloride as dough strengthening and raising agent and also as preservative and as an emulsifier, texturiser and astringent in cosmetics ; and sodium phosphate as texturizer to change the appearance of

food, neutralizing agent, nutrient as well as leavening agent to help dough rise and in cosmetics as buffering agent and as fragrance ingredient and sodium sulphate as cleanser and skin care products.

But one of the most important property of these inorganic electrolytes apart from those listed above is that they also lower the interfacial tension and stabilize the formation of emulsions. But they cannot be used alone as they form only o/w type emulsions with short life times (Sherman et al. [3]). But when they are used along with surfactants the interfacial tensions of different systems show an interesting behaviour. The studies on the effect of electrolytes on interfacial tension in field of oil recovery are extensive but it lacks research when it comes to dietary oils.

There is not much but contrasting data available on interfacial tension behaviour in presence of salt. Due to inorganic electrolytes present in the aqueous phase, the water molecules form a hydrogen bonded structure around the elctrolyte ions. However the presence of oil phase at the interface breaks the hydrogen bonding thus increasing the energy. This leads to depletion of salt ions and hence the surface excess concentration of salt ions become negative. Thus according to Gibbs adsorption isotherm, interfacial tension should increase when inorganic salts are present in the aqueous phase.

Contrasting to above trend decrease in interfacial tension on increasing the concentration of electrolyte has also been reported. Many mechanisms are reported in literature for this effect. Yarranton et al [4] suggest that increase in concentration leads to increase in activity coefficient of surfactant molecule which leads to lower interfacial tensions. Salt scatters the surfactant molecules between oil and aqueous phase and leads to increase in adsorption of surfactant at the interface.

CHAPTER 2

LITERATURE SURVEY

2.1 Introduction:

It is the amphiphilic character of surfactants that make them suitable for a large number of applications such as oil recovery, drug delivery, detergency, froth floatation, etc. They contain a hydrophilic part which remains in the water and a hydrophobic part which tends to remain in the oil or air. The adsorption of surfactants on interface is of importance for the stability of foams and emulsions.

Thus knowledge of microsturctures of microemulsions is of great importance. Quite good amount of literature is available that relates the microemulsion structure and physical properties. But for complete interpretation, a combination of different techniques is required.

Table 2.1 Previous studies on microemulsions

Reference	**Microemuslsion System**	**Characterization Parameters**	**Applications**
Kaurr et al. [5]	Brij 96/ ethlyl oleate/ butanol	Viscosity, cyclic voltammetry, DLS, NMR	Cosmetics, Drug Delivery
Singh et al. [6]	Soyabean oil/ Phospholipids, Soyabean oil /ethoxylated mono and di-glycerides	Phase diagram, DLS, Cryo-SEM	Food Grade Emulsions
Aramaki et al. [7]	Sucrose dodecanoate/ decane	Phase diagram, Small angle X-ray Scattering	Phase behaviour of cubic microemulsions
Faunn et al. [8]	Peppermint oil/ Ethoxylated mono and di-glycerides	Phase diagram	Food grade micromemuulsions
Li et al. [9]	n-octane/CTAB/ 1-butanol	Phase diagram (Solubility), Conductivity	Iron nanoparticles production
Lago et al. [10]	n-decane/ trihexyl (tetradecyl) phosphonium chloride	Microscope, Phase diagram (Gas Chromatography)	Enhanced oil recovery

The formation of microemulsions is influenced by the interfacial tension and hence their free energy depends on bending energy of surfactant monolayer by which structural features of microemulsions can be easily interpreted. Cationic, anionic and non ionic surfactants have been used in literature to decrease the interfacial tension and thus increase the stability. However, if the electrolytes are used along with surfactants the interfacial tension is further influenced which reduces the consumption of costly surfactant.

2.2 Interfacial tension of oil water interface:

Microemulsion term was proposed by Jack H. Schulamn in 1959. According to him a stable oil-rich mixture can be converted to a stable water-rich mixture and this is called a microemulsion (Schulman et al. [11]). Microemulsions are thermodynamically stable systems and have numerous practical applications. According to Flanagan et al. [1], microemulsion characterization can be divided into two main areas, i.e. characterization at the microscopic and macroscopic levels. The interfacial tension represent the macroscopic level measurements. For a fine emulsions it is important for solubilisation to be large and interfacial tension to be very low. In other words, interfacial tension is an important property. It characterises the quality of an oil (Gertz et al. [12]). An insight into literature shows measurement of this property limited to only hydrocarbons because of their application in enhanced oil recovery.

Table 2.2 Previous studies on IFT of hydrocarbons.

Reference	**Interfaces**	**Conditions**	**Methodology used**	**Remarks**
Langevin et al. [13]	Toulene/water, Butanol/ water	SDS, CTAB	Surface laser light scattreing	Correlation between surface bending elasticity and the structure of the microemulsion phases and the IFT.
Shinoda et al. [14]	Hexadecane/water	Lecithin	Spinning drop tensiometer	Effect of HLB on phase stability and IFT.
Gassin et al. [15]	Dodecane/water	TX-100	Pendant Drop technique	Quantification of interfacial transfer

				mechanism factors based on diffusion controlled adsorption desorption mechanism.
Jasper et al. [16]	C_5 , C_6, C_7, C_9 alkylbenzenes/ Water phase	No surfactant	Drop volume method	Antonov's rule applies only to a limit for a homologous series of hydrocarbon-water system
Yang et al. [17]	n-nonane/ water, crude oil/water	Hexadcylbenzene sulphonate as surfactants	Spinning Drop tensiometry	Effect of location of benzene rings in surfactant is studied.
Zhang et al. [18]	n-octane/water	Surfactant: 1-Phenyltetradecane sulphonate, and Fatty acids: Lauric acid, Plamitic acid.	Spinning Drop tensiometry	Appropriate concentration ratios of phenyltetradceane sulphonates and fatty acids produce synergism for surfactant adsorption
Ahmedi et al. [19]	Kerosene oil/ water	Mulberry leaf extract	Pendant drop method	Environment friendly surfactant with 60% efficiency
Geordias et al. [20]	(n-decane + CO_2)/ water	No surfactant, Pressures upto 50MPa	Wilhmey plate technique	(n-decane + CO_2) system becomes miscible at elevated temperature and pressure.

But microemulsions are also equally important in cosmetics, food and pharmaceutical industry. First study on interfacial tension of vegetable oil/water was done by Lord Rayleigh in 1890.

The first study for surface active effect of monoglycerides present in soyabean oil was done by Kako et al. [21]. They related the maximum in stability of oil globule to the ratio of fatty acid groups in monoglyceride and di glycerides.

Gaonkar et al. [22] studied the effect of interfacially active components present in vegetable oils. He measured IFT of purified soyabean and corn oil against impure oils and concluded that the monoglycerides present in vegetable oils acts as surface active components. The trend followed by interfacial tension. In another study by Gaonkar et al. [23] they concluded that vegetable oils contain other impurities also which are more surface active then the monoglycerides. Also after their work only it was concluded that monoglycerides lead to formation of reverse micelles in oil. The trend followed by IFT for different amounts of monolglyceride content is shown in figure 2.1.

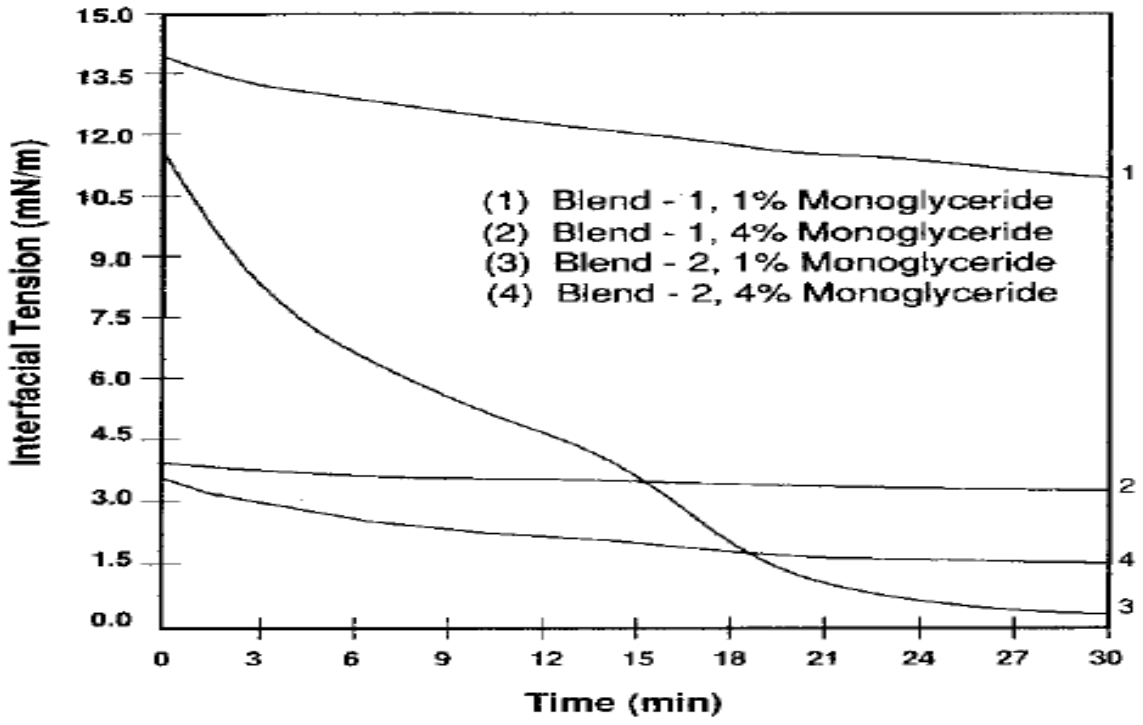


Figure 2.1 Interfacial activity of monoglycerides as a function of 4.5% NaCl at 50° C for soyabean oil water interface (Gaonkar et al. [23]).

After his study lot of research has been done on vegetable oils to evaluate the effect of oil purification on interfacial tension.

Miller et al. [24] studied dynamic interfacial tension of various dietary oils as olive, linseed and pumpkin oil using drop volume tensiometry technique. In their work it was documented that these oils contain natural surfactants also as the results they obtained with virgin oils were different from the one when they purified the oil. So they suggested that some components present in these oils have property to lower the interfacial tension.

More recently Ferrari et al. [25] studied the surface properties of coffee oils for the first time. Coffee oils have a large number of applications as in food industry for flavouring and also in biodiesel production. They collected samples from India and Brazil. They came out at an important conclusion that like other vegetable oils, coffee oils also show different interfacial behaviour when caffeine is removed from them. They concluded that caffeine acts as natural surfactant in raw coffee seeds.

Interfacial phenomenon has also been suggested to affect the characteristics of fried food. Gil et al. [26] related the increase in oil absorbance of doughnuts after repeated frying to the lower interfacial tension of frying fat/ water interface. Kalogianni et al. [27] has determined the effect of deep fat frying on the interfacial tension of palm oil and olive oil.

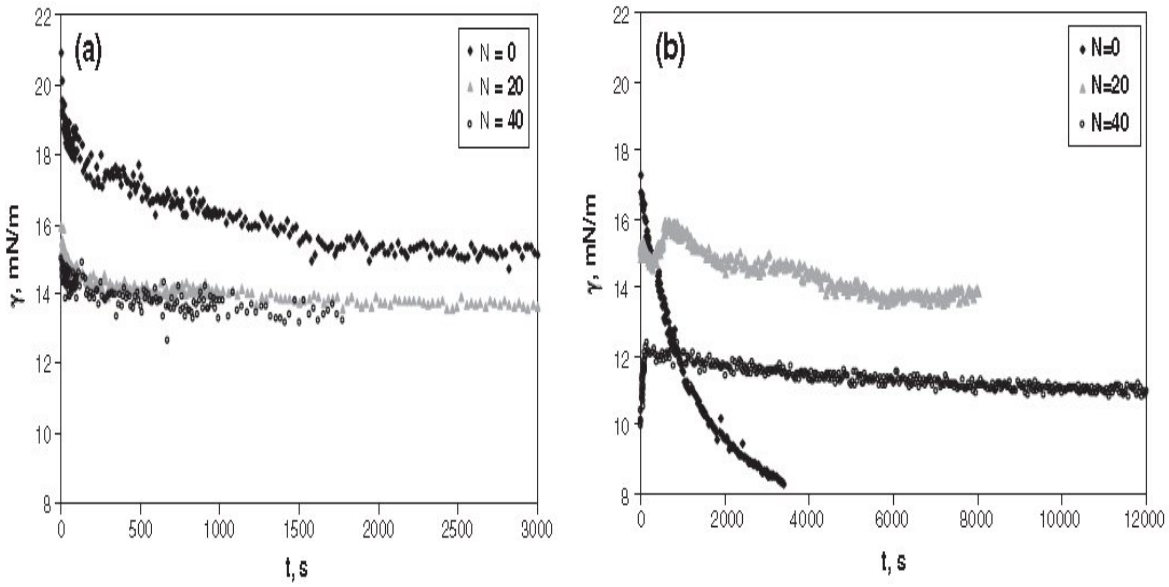


Figure 2.2 Palm oil and olive oil IFT against water as a function of time (t) and frying batch number (N). (Kalongianni et al. [27])

They observed trend as shown in figure 2.3 for interfacial tension for both oils is different which was due to formation of different compounds in each oil during frying.

Surfactants are usually prepared from chemical that are harmful to environment. Research is still on for biocompatible and biodegradable surfactant molecules. Ampatizidis et al. [28] have recently studied phenyl and tyrosine- glycerol ether surfactants for eco-friendly cosmetic emulsions. Their work includes activity studies of olive oil/ water interface in presence of above biocompatible molecules dissolved in organic phase and Tween 20 in aqueous phase. $PhGE_{12}$ attains comparatively lower interfacial tension in their system and can be considered for application in cosmetic emulsions for example cleaning fluids, personal hygiene creams, etc.

2.3 Effect of electrolyte on interfacial tension of oil water interface:

The electrolytes when used in emulsion systems affect the colloid chemical properties of surfactant molecules which makes their study interesting. There has been evidence of adding non-organic salt in systems of surfactant for enhanced oil recovery. While with electrolytes in aqueous solutions the surface tension increases but when used with surfactants the interfacial tension has been reported to decrease by many authors. Data for the effect of salt on interfacial tension is contrasting. Cai et al. [29], Bakes et al. [30] observed increase in IFT values on addition of salt whereas Alotaibi et al. [31], Saldana et al. [32] found decrease in IFT values on addition of salt. Koelsch et al. [33] has investigated the effect of an inorganic electrolyte on adsorption of a cationic soluble surfactant using surface tension and ellipsometry techniques. They found that a phase transition occurs between free counterions and counterions in diffuse layer with an increase in bulk concentration. The difference in CMC and surface excess with concentration for the surfactant solution and solution containing electrolytes was thought to be due to the change in structure of water molecules at the interface.

In a study on adsorption of anionic surfactant on the interface of water/ hexane, water/heptanes and water/toluene by Moradi et al. [34], the effect of temperature and increasing salt concentration in adsorption parameters was studied. They used conductometric technique for examining surfactant/water/oil systems. Their results show that the existence of sodium bromide and decreasing temperature decreases both the CMC and surface tension.

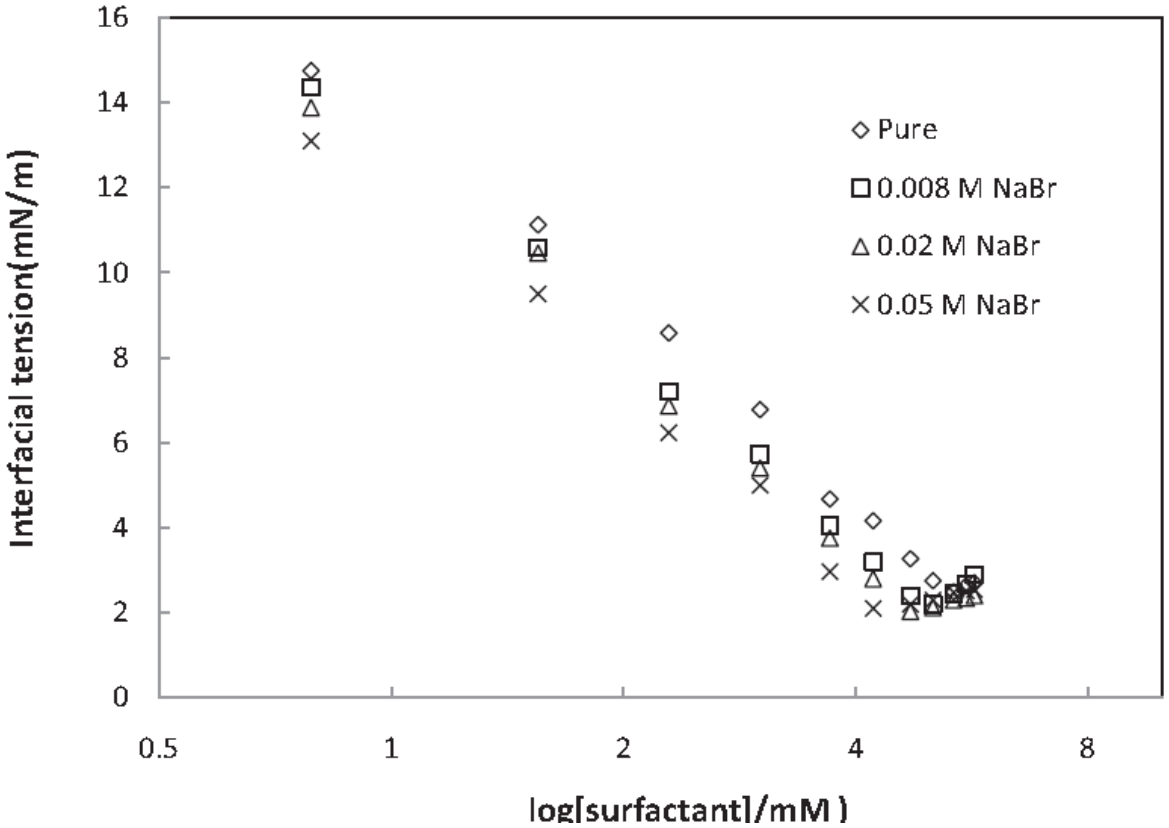


Figure 2.3 Salt effect on interfacial tension (Moradi et al. [34]).

Dikhtievskaya et al. [35] have studied the effect of electrolytes; sodium, calcium and aluminium chlorides on the interfacial tension of several oil phases as hexane, octane, decane, dodecane, rapesedd and olive oils in presence of sodium alkyl sulphates and alkyl carbonates as surfactants. They concluded that various factors like nature of surfactant and oil phase, and presence of various factors influence the IFT and hence the emulsification process.

In an attempt by Inavov et al. [36], a theory accounting for the effect of counterions on the adsorption constant was proposed. They calculated experimental K values by using interfacial tension isotherms. Also an attempt was made by them to calculate the disjoining pressure isotherm for the films stabilized by different counterions.

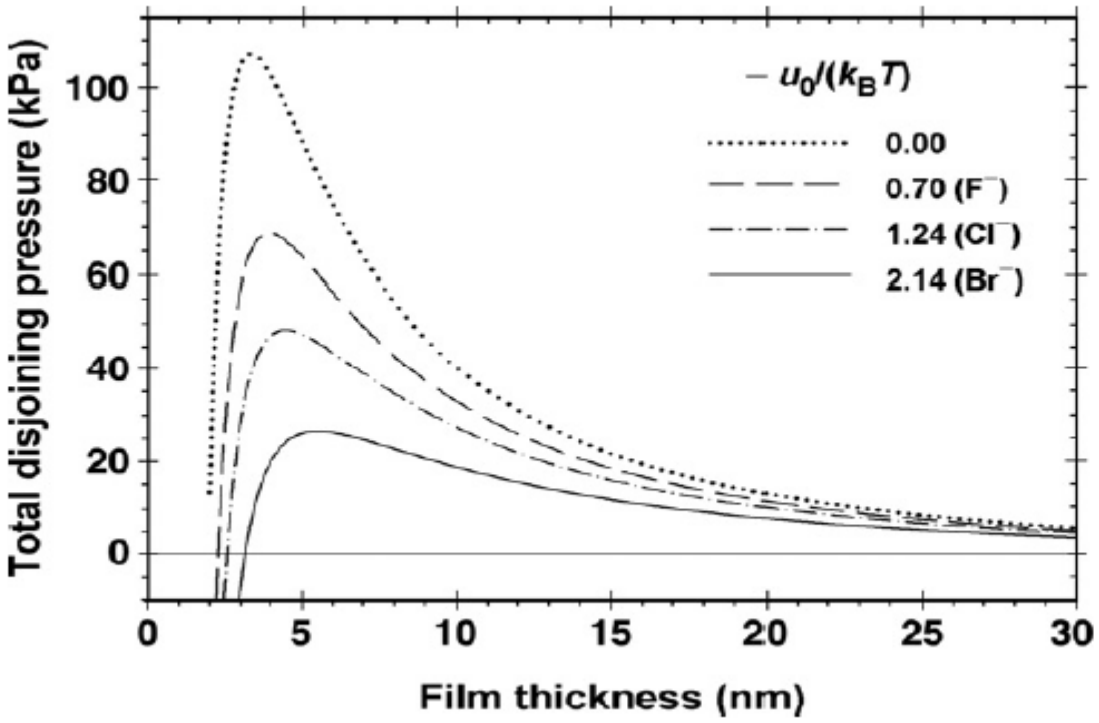


Figure 2.4 Total disjoining pressure calculated for different counterions (Inavov et al. [36]).

From the above figure they concluded that the effect of counterions is most significant for films of small thickness.

Li et al. [9] investigated the effect of NaCl, $CaCl_2$ and $MgCl_2$ on the interfcial tension of fatty alcohol polyoxyethylene carboxylate against alkanes. They found NaCl to be least effective in reducing the IFT and proposed a mechanism for the same. The model provided by them includes the partitioning of surfactant into oil phase and the decreased charge repulsive force between surfactant molecules.

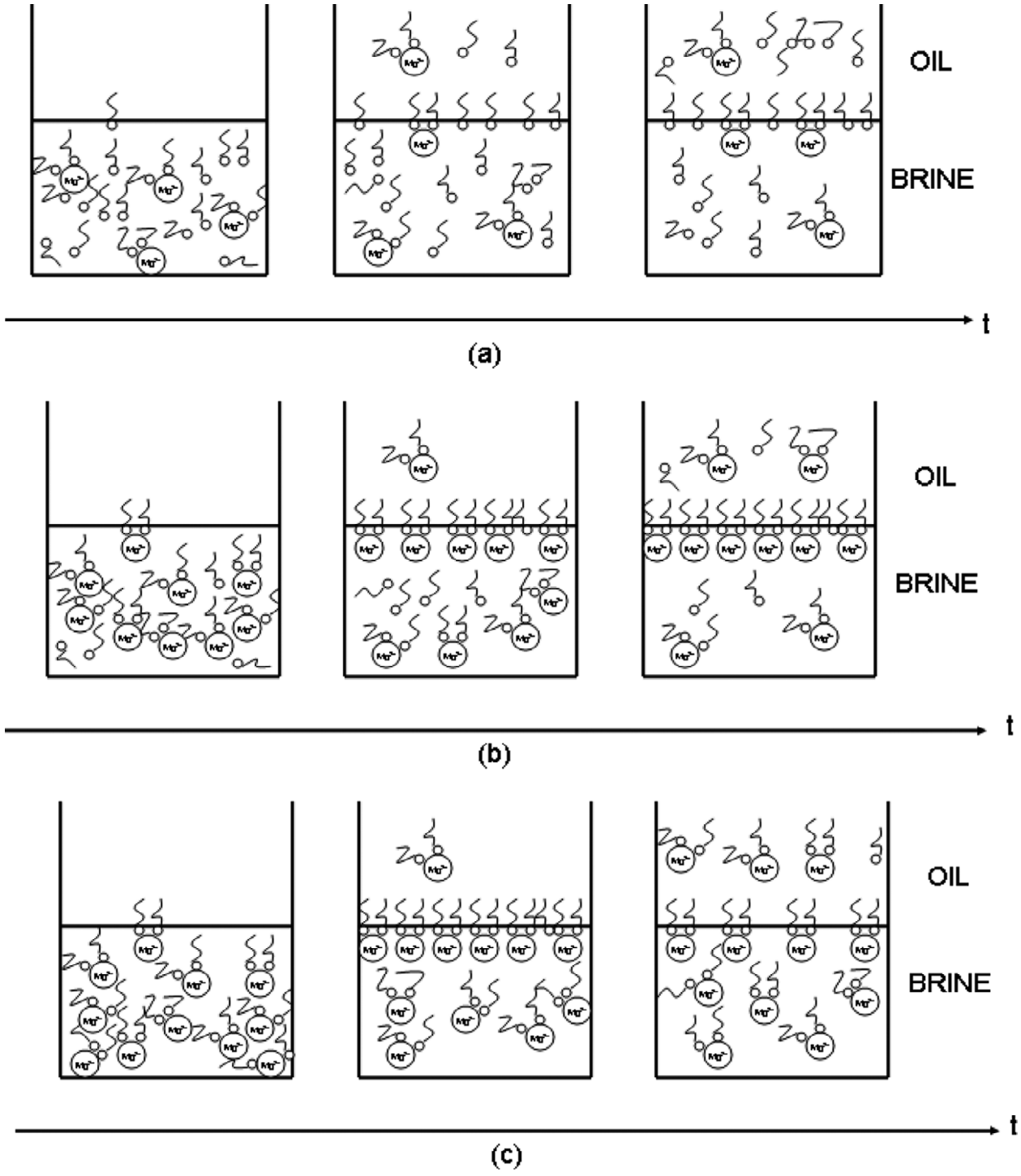


Figure 2.6 Proposed mechanism for effect of electrolytes on IFT (Li et al. [9])

Gaonkar et al. [26] investigated the effect of salt and temperature on interfacial tension of soyabean oil water interface from the point of its application in food emulsions. He found the IFT to decrease with increase in salt content. He attributed this behavior to the increase in interfacial activity of rinoleic type molecules impurities found in soyabean oil.

2.4 Motivation of the project:

Vegetable oil contain small amount of toxic elements and are renewable, easily available and non polluting energy resources. So they have been used for a lot of other purposes also such as biodiesel production, production of hydrocarbons by catalytic pyrolysis, etc. Sunflower oil is commonly used as a cooking oil. It is produced from sunflower seeds using the process of cold press. It contains low amount of saturated fats and high amount of linoleic acid. It also possess high vitamin E content. Vitamin E has potential health benefits such as its ability in preventing damage to sensitive skin cells by the harmful ultraviolet light from the sun.

2.5 Overview of the project:

Interfacial tension plays a significant part in formation of microemulsions as they have a large number of properties as drug solubility, thermodynamic stability which are important in pharmaceutical, food and cosmetic industries. The main objective of the project is to study how electrolytes influence the interfacial tension.

1. To compare the interfacial tension trend of sunflower oil -water interface in presence and absence of surfactant.
2. To study how the interfacial tension is changed in presence of different electrolytes viz. Sodium chloride, calcium chloride sodium sulphate and sodium phosphate.
3. To study how the concentration of electrolytes affect the interfacial tension
4. To find the surfactant adsorption in case of above electrolytes.

CHAPTER 3

EXPERIMENTAL WORK

This chapter gives an overview of the experimental methods and experimentation followed in the project. The interfacial tension measurements were done using Du-Nuoy ring tensiometer at ambient conditions of temperature and pressure. The interfacial tension values were measured over some time using the instrument.

3.1 Materials

The measurement of interfacial tension requires the presence of an organic phase and an aqueous phase. The organic phase used was commercial refined sunflower oil of Dalda brand.

Aqueous phases were prepared from double distilled water, surfactant and different salts. The salts used were: sodium chloride, calcium chloride dihydrate and sodium di-hydrogen phosphate. All salts were purchased from Sigma Aldrich. The surfactant used was cetyltrimethyl ammonium bromide (CTAB, purity >99%). Anhydrous Ethanol was from Merck. All reagents were used as received without further purification. Ethanol was used for cleaning purposes.

3.2 Properties of Surfactant Used

Cetyltrimethylammonium bromide is a cationic surfactant with molecular weight of 364.5g/mol and molecular formula $(C_{16}H_{33})N(CH_3)_3Br$. It is soluble in water and has high tolerance for salts. It has molecular structure as shown in figure 3.1. The CMC value for CTAB is 0.98 mM or 0.357 g/l.

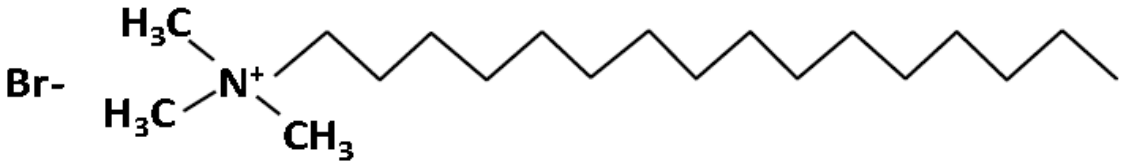


Figure 3.1 Molecular Structure of CTAB.

3.3 Interfacial Tension Measurements

3.3.1 Principle of Du Nuoy Ring Tensiometer

The Du Nuoy ring method is a simple method but require careful hands to measure the interfacial tension as the ring is very delicate. Equilibrium interfacial tension measurements at oil water interface were done with a Pt-Ir ring on a surface tensiometer (Dataphysics, Filderstadt, Germany, DCAT 11EC) which is shown in figure 3.1.

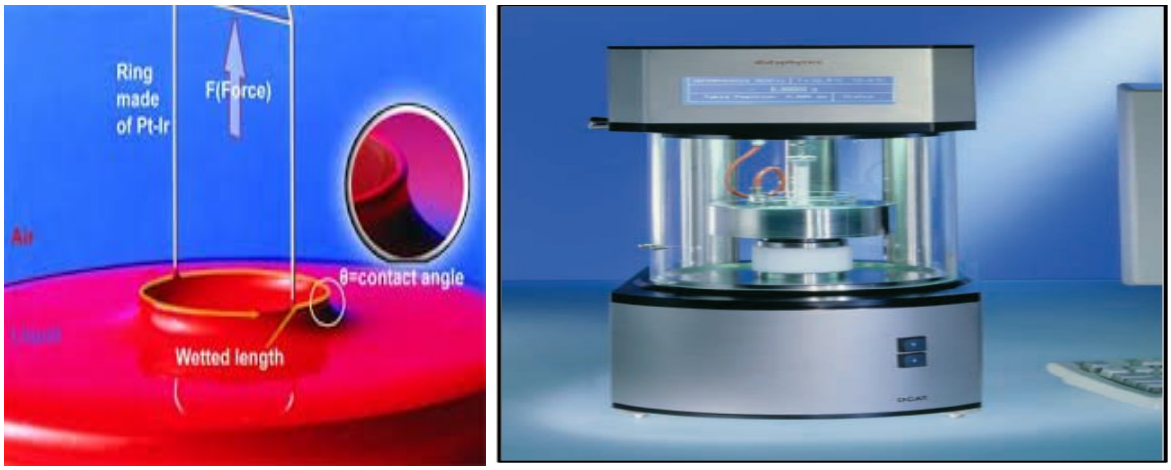


Figure 3.2 Du Nuoy ring tensiometer

It works on a detachment technique i.e. the interfacial tension is measured by measuring the maximum force required to separate the ring from contact with interface. Then the force acting on ring as it pierces the interface during detachment from liquid is measured by using tensiometer having an inbuilt microbalance. By measuring this force the interfacial tension can be calculated using the relation given by

$$\gamma = \frac{F}{4\pi r}$$

The platinum ring was fully rinsed with water followed by alcohol and flamed before and after each measurement.

3.3.2 Procedure of Interfacial Tension Measurement

Preparation of solutions

The surfactant stock solution was prepared by exactly weighing and dissolving in appropriate volume of water and shaken till completely dissolved. The salt solutions were also prepared in similar manner. The lower concentrations were prepared by diluting the stock solutions.

Measurement of interfacial tension

The ring was carefully cleaned and put into the probe. The instrument was used on pull method which requires addition of light phase to heavier phase. The aqueous phase was first put into the vial and then oil phase was carefully added to it using a dropper. Utmost care needs to be taken while adding oil phase so that the two phases do not mix and also the ring is not deformed. Then the interfacial tension was recorded till an equilibrium value was reached.

CHAPTER 4

EFFECT OF ELECTROLYTES ON INTERFACIAL TENSION OF SUNFLOWER OIL WATER INTERFACE IN PRESENCE OF CTAB

4.1 Introduction

Surface tension exists between any two different surfaces, which can be either fluid-fluid or solid-fluid. In the case of fluid- fluid, it is better called interfacial tension.

The measurement of interfacial tension can be done either by any of the methods available in literature. While Wilhmey plate and Du-nuoy ring techniques are known for equilibrium surface tension measurement, drop and bubble profile tensiometry are useful in case of dynamic measurements. In this chapter interfacial tension data on oil/surfactant and oil/electrolyte/surfactant are presented and hence the effect of electrolytes on interfacial tension is summarised.

4.2 Results and Discussion

4.2.1 Dynamic Interfacial tension of sunflower oil water interface

Fig.4.1 shows the dynamic interfacial tension of sunflower oil water interface.

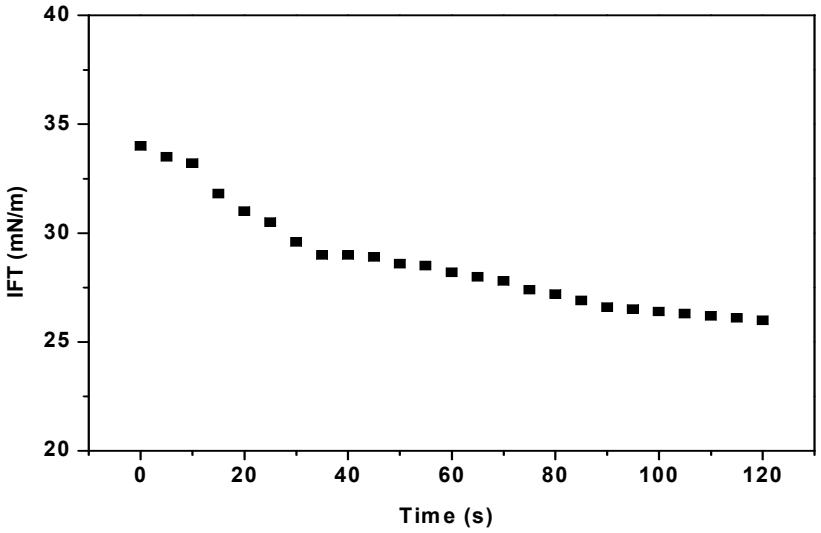


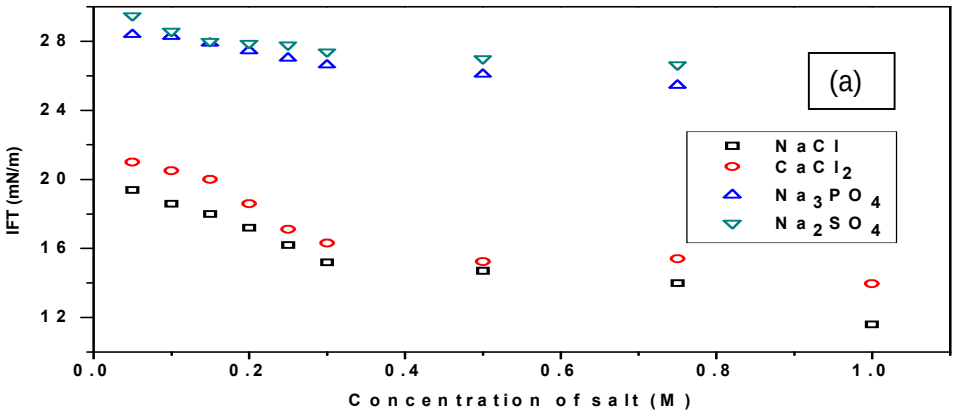
Figure 4.1 Dynamic interfacial tension of sunflower oil water interface.

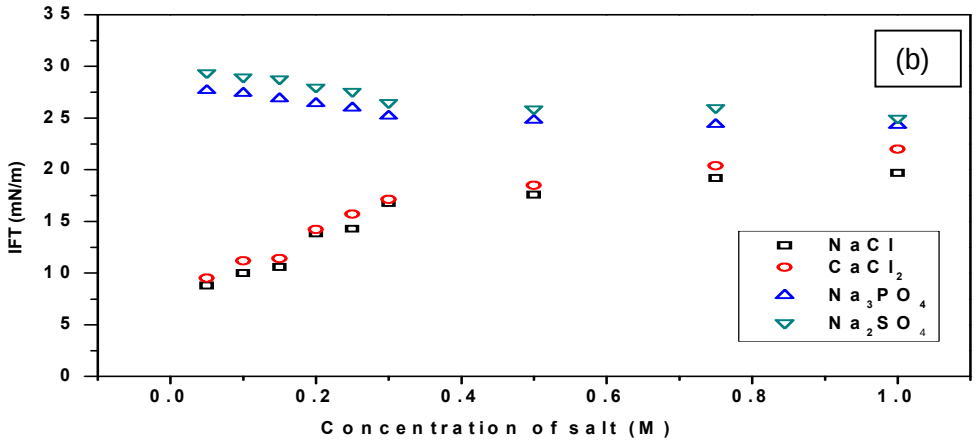
The measurement is done using Du-nuoy ring tensiometry. The fastest decrease is obtained initially suggesting the presence of surfactants such as mixture of monoglycerides but after around 110 seconds partial equilibrium is attained. The equilibrium is attained faster with ring tensiometry technique when compared to other techniques as shown by Stubenrauch et al. [37]for surface and interfacial tension of CTAB solutions with different chain length of CTAB. They attributed this effect to the convective currents caused by motion of ring. The equilibrium value

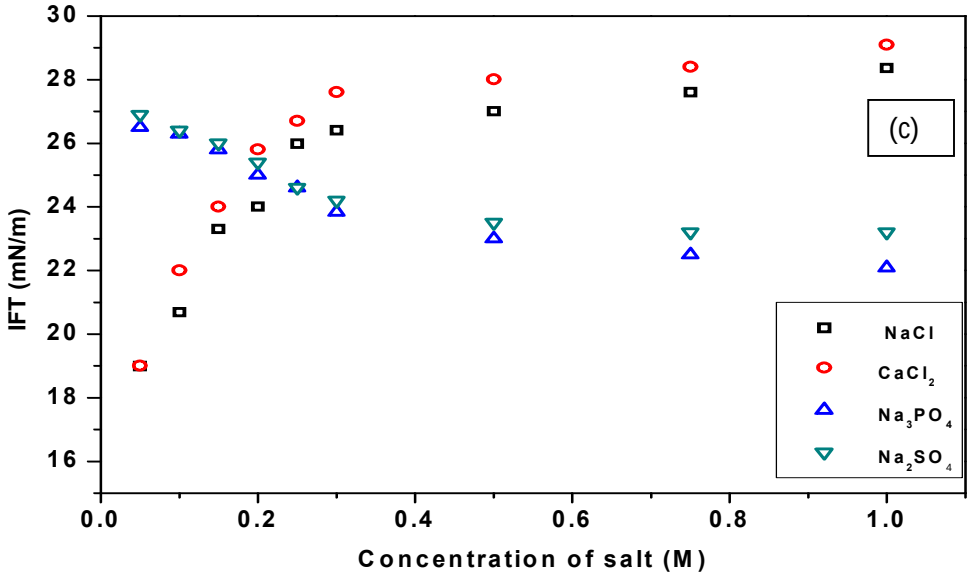
for interfacial tension of a plane sunflower oil water interface comes out to be 29mN/m. This is slightly higher from some values reported in literature as 26mN/m. This may be due to the fact that the oil used by us is refined oil and the process used by the manufacturer may have removed the natural components such as free fatty acids, mono and di-aclyglycerols present in sunflower oil which otherwise acts as natural surfactants to some larger extent.

4.2.2 Electrolytes effect on interfacial tension at constant concentration of CTAB.

Firstly the change in interfacial tension for a particular surfactant concentration with increasing electrolyte concentration is studied and plotted in figure 4.2. Four different electrolytes viz. NaCl, $CaCl_2$ and Na_3PO_4 and Na_2SO_4 were used in study.







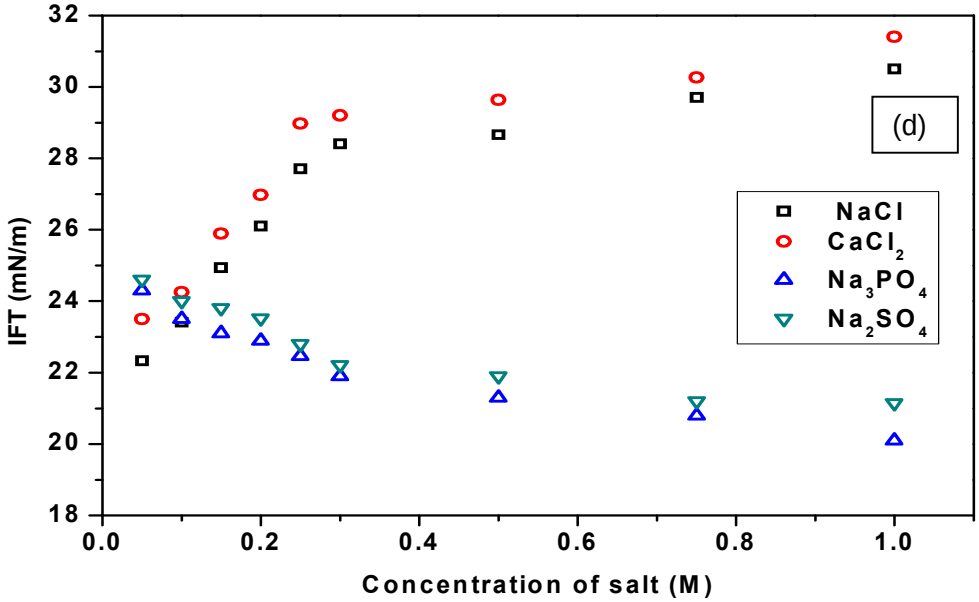
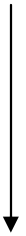


Figure 4.2 Effect of increasing electrolyte concentration at fixed concentrations of surfactant (a) 0.01 mM CTAB, (b) 0.1 mM CTAB, (c) 1 mM CTAB, and (d) 10 mM CTAB.

These results can be further summarized as shown in Table 4.1

Table 4.1 Trend followed in interfacial tension at different constant concentrations of electrolyte (Size of arrow is an indicator of value of interfacial tension).

	Concentration of CTAB			
Electrolyte	**0.01 mM**	**0.1 mM**	**1 mM**	**10 mM**
Sodium Chloride				
Calcium Chloride				
Sodium phosphate				
Sodium sulphate				

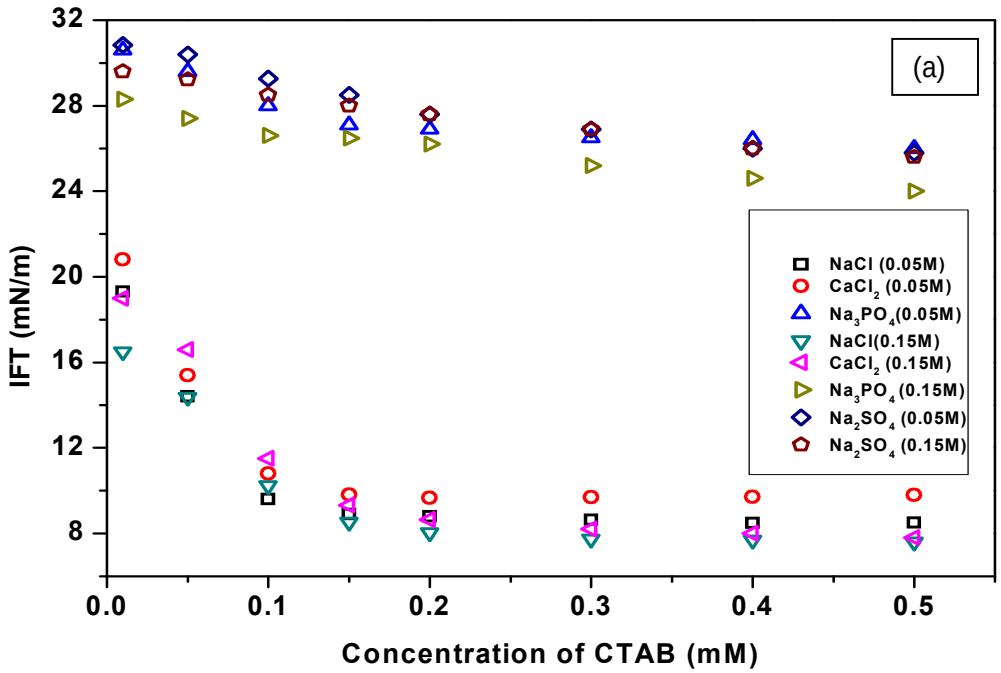
From the graph it is observed that when the concentration of CTAB is much less then CMC IFT decreases with increase in concentration of salt for all salts. And lowest interfacial tension is obtained for NaCl. The salts NaCl, Na_2SO_4 and Na_3PO_4 will dissociate to give same cation Na^+ but differently charged anions. However against the expected trend that more negatively charged anion should give lowest interfacial tension based on electrostatic nature, a contrasting trend is

observed for the interfacial tension. The trend observed for the above can be classified as ion specific nature based on Hofmeister series. Chloride ions are placed near the hydrophobic end of Hofmeister series so they are more effective in screening the electrostatic repulsion between CTA^+ cations adsorbed in the monolayer. But PO_4^{3-} and SO_4^{2-} ions are located at the hydrophilic end of Hofmeister series, so the electrostatic repulsion screening is less.

At higher concentrations of CTAB, the coions i.e. the ions charged similarly to surfactant ion may penetrate into the surfactant adsorption layer due to latent coagulation phenomenon and repel the surfactant ions. So the interfacial tension starts increasing for the chloride ion. However, the phosphate and sulphate ions due to their larger valency does not allow the Na^+ for penetration but they themselves if present on the interface may lead to saponification of fatty acids present in oil further lowering the interfacial tension.

4.2.3 Surfactant effect on interfacial tension at constant concentration of electrolytes.

After the effect of constant concentration of surfactant was studied, effect of surfactant at constant concentration of electrolytes was studied. For all the three electrolytes two concentrations of 0.05M and 0.15M were used. The results are plotted in figure 5.3.



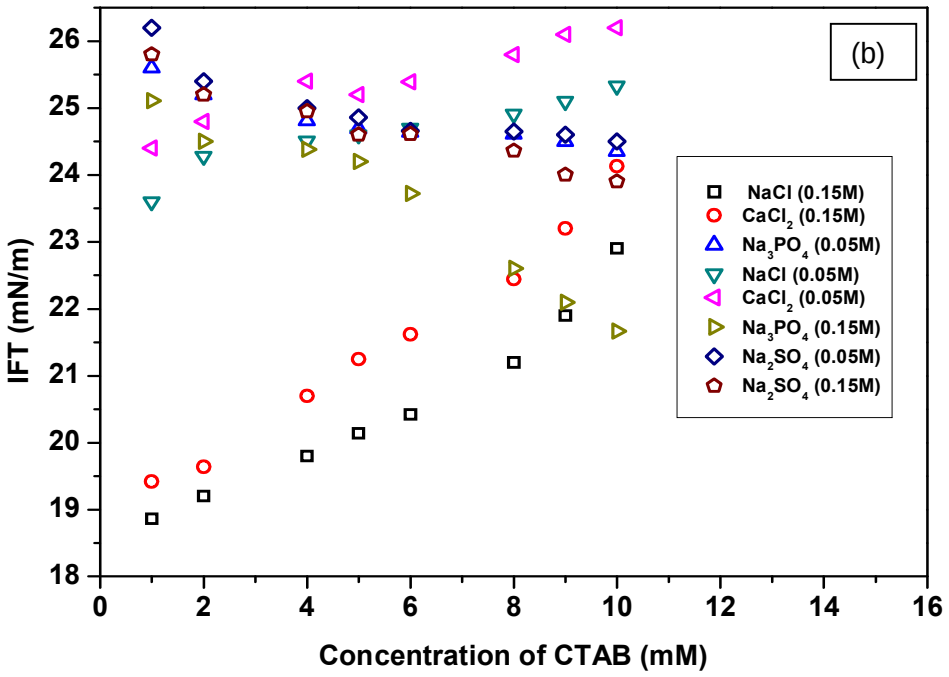


Figure 4.5 IFT variation at fixed concentration of electrolyte (a) when concentration of CTAB is varied below CMC, (b) when concentration of CTAB is varied above CMC.

The trend followed can be summarized as in Table 4.2.

Table 4.2 Trend followed by interfacial tension at a fixed concentration of salt.

Electrolyte	**Concentration of electrolyte**	
	0.05 M	**0.15 M**
NaCl	↓	↓
$CaCl_2$	↓	↓
Na_3PO_4	↓	↓
Na_2SO_4	↓	↓

From the above it is interpreted that lower interfacial tensions are observed at higher electrolyte concentrations. This trend has been also reported by Reynders et al. [38]. This is attributed to the electrostatic contributions to the surface pressure by electric double layer. For dilute surfactant

solutions, the interfacial tension trend is in accordance with Hofmeister series but for concentrated surfactant solutions, different trends are observed due to latent coagulation phenomena.

CHAPTER 5

EFFECT OF ELECTROLYTES ON SURFACTANT ADSORPTION AT INTERFACE

5.1 Introduction.

At the interface whether solid-liquid or liquid-liquid, the amount of surfactant adsorbed per unit area of the adsorbent needs to be determined as this is a measure of the efficiency of surfactant. An adsorption isotherm is a quantitative measure of the amount of adsorbate at the interface to its equilibrium concentration in the bulk. There are a number of adsorption models to describe the adsorption behavior. In this chapter we have studied the surfactant adsorption using different adsorption models.

In liquid-liquid or liquid-gas systems it is difficult to isolate or measure the interfacial region from bulk phase. So in these systems the amount of adsorbate per unit area of interface is calculated indirectly from surface tension data. Hence in these systems, plot of interfacial tension versus concentration of surfactant is used to calculate surfactant adsorption. A number of equations have been suggested that relate the amount of surfactant at interface to surface tension and its concentration in bulk phase at equilibrium.

5.2 Results and Discussion

5.2.1 The Langmuir Adsorption Isotherm.

Langmuir adsorption model was firstly developed for adsorption on solid surface. But it can be significantly used for adsorption on liquid interfaces with some conditions as that there are no intermolecular interactions and the adsorption film is monolayer. Many surfactant solutions follow the Langmuir type isotherm given by:

$$bc = \frac{\omega}{1 - \omega}$$

Where = the surface concentration of surfactant, in mol/cm^2 at monolayer adsorption

c= concentration of surfactant in liquid phase at adsorption equilibrium

b= a constant

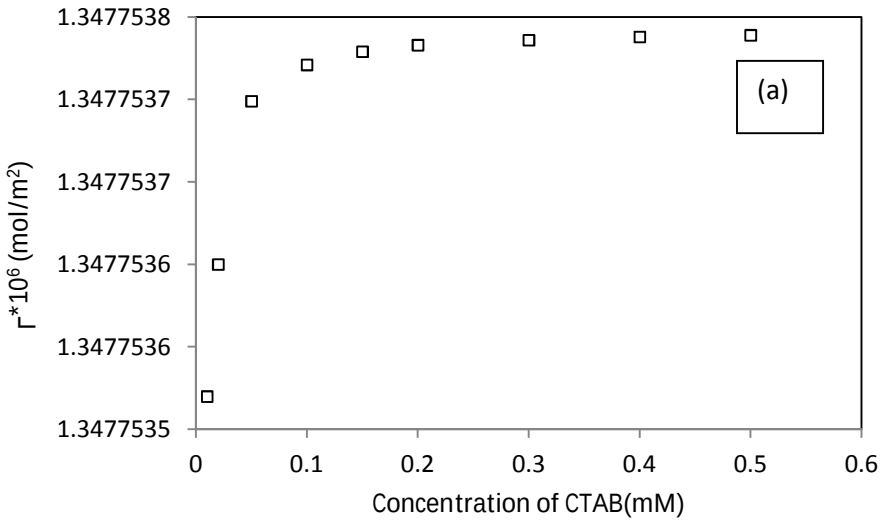
ω = area covered by one molecule in surface layer.

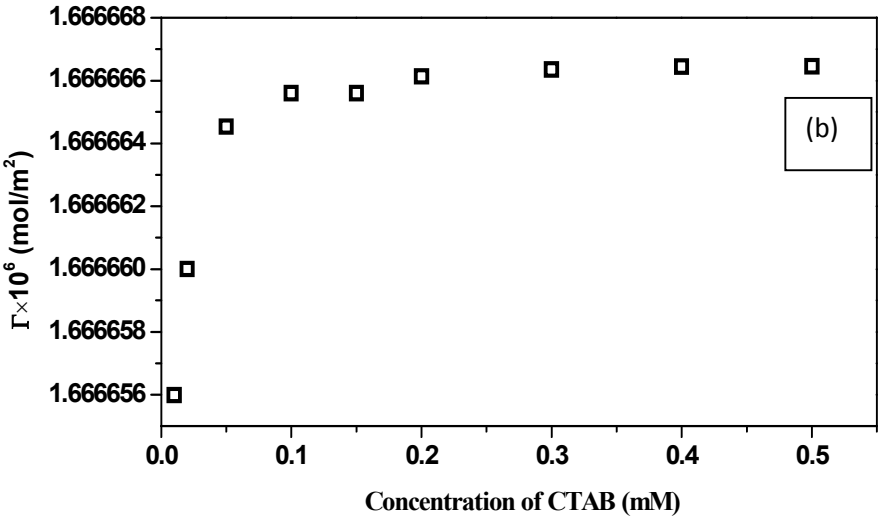
The experimental data was fitted with Langmuir adsorption model using Isofit. It was observed that it is possible to fit the experimental data with Langmuir model quite well. But it does not mean that the assumption on which Langmuir model is based is fulfilled. Parameters of adsorption layer obtained with Langmuir model at the interface are shown in Table 5.1.

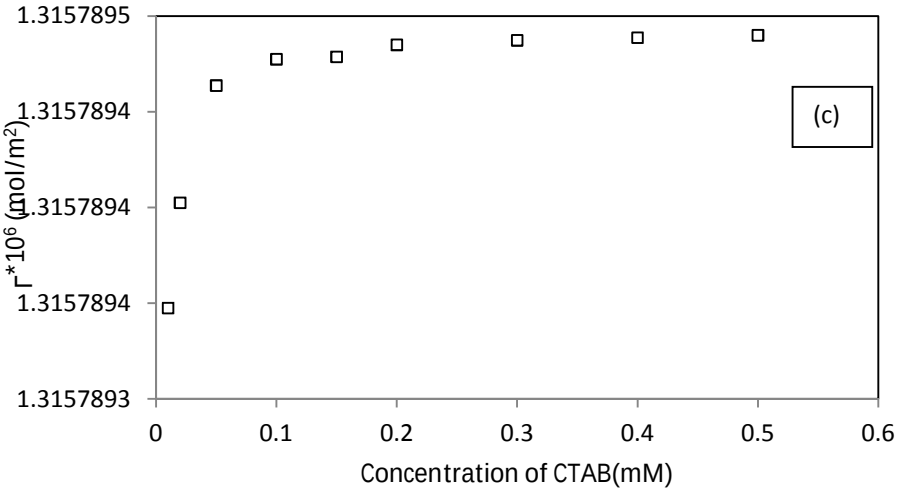
Table 5.1 Parameters of adsorption layer obtained with Langmuir model at sunflower oil water interface.

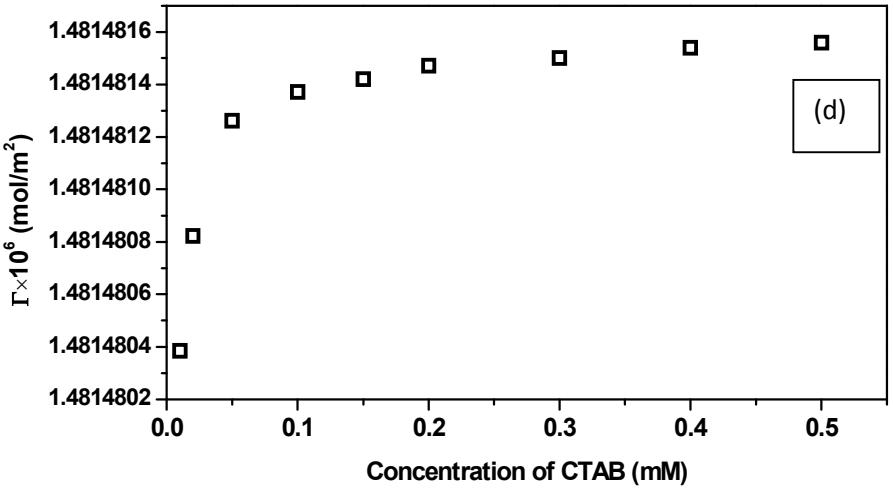
S.No.	Electrolyte	Concenteration of electrolyte	€(%)	a	b(1/mmol)	ω(m^2/mol)
1	NaCl	0.05 M	3.45	0	$1.14*10^8$	$6.40*10^5$
2	$CaCl_2$	0.05 M	2.88	0	$1.56*10^7$	$6.8*10^5$
3	Na_3PO_4	0.05 M	2.75	0	$4.22*10^6$	$9*10^5$
4	Na_2SO_4	0.05 M	4.65	0	$4.05*10^6$	$9.8*10^5$
5	NaCl	0.15 M	2.95	0	$1.64*10^8$	$5*10^5$
6	$CaCl_2$	0.15 M	6.69	0	$1.35*10^8$	$6.60*10^5$
7	Na_3PO_4	0.15 M	7.83	0	$6.01*10^6$	$7.4*10^5$
8	Na_2SO_4	0.15 M	5.86	0	$4.2*10^6$	$8*10^5$

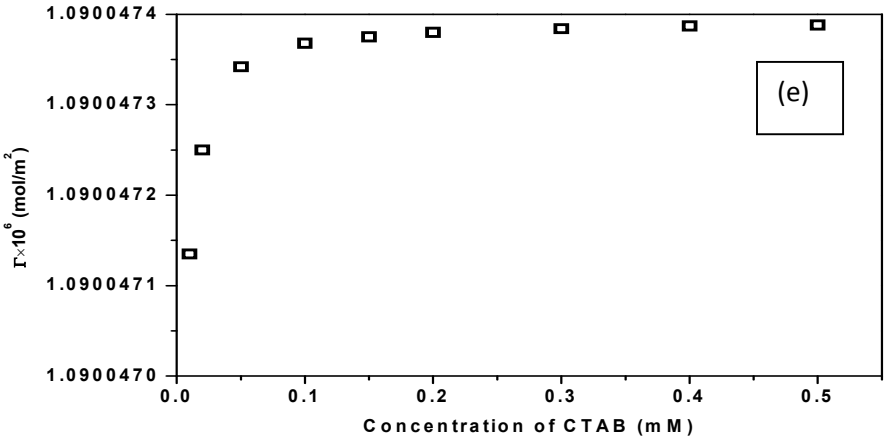
The 'b' and 'ω' values in all cases are quite close to each other however the molar area 'ω' is highest for 0.05 M Na_3PO_4 and lowest for 0.15 M NaCl. The value of 'a' for Langmuir Model in all cases is zero. The surfactant adsorption was calculated from the values in Table 5.2. The results are plotted in Figure 5.1 individually.

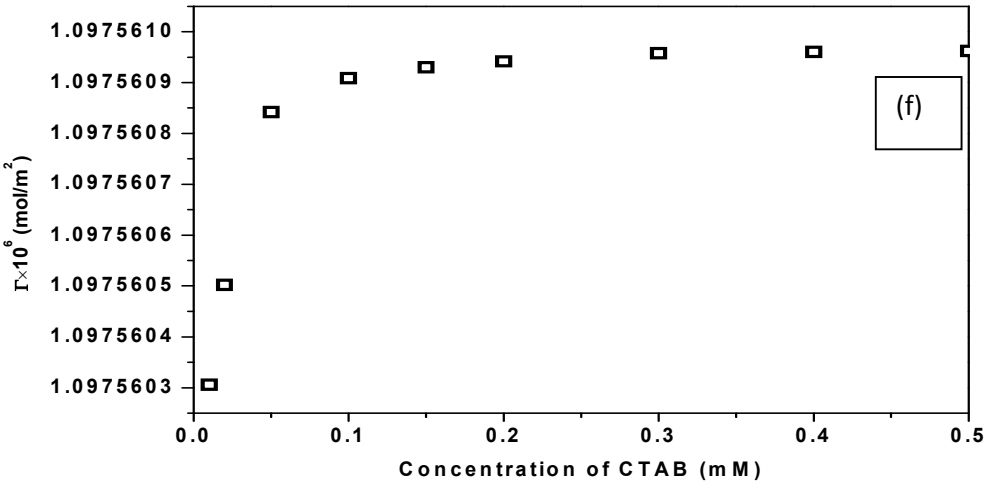


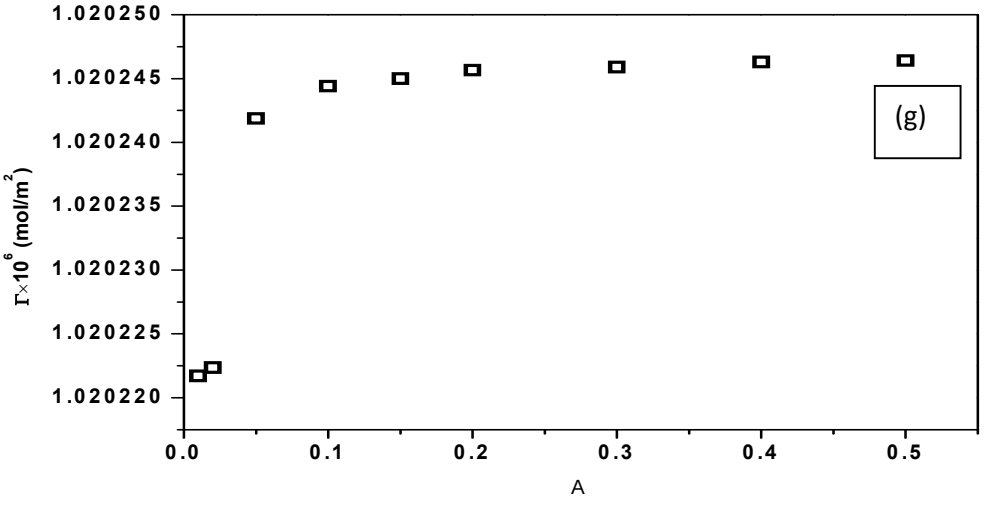

1.666668
1.666666
1.666664
1.666662
1.666660
1.666658
1.666656
Γ×10^6 (mol/m^2)
(b)
0.0
0.1
0.2
0.3
0.4
0.5
Concentration of CTAB (mM)


1.3157895
1.3157894
1.3157894
1.3157894
1.3157893
Γ*10^6 (mol/m^2)
(c)
0
0.1
0.2
0.3
0.4
0.5
0.6
Concentration of CTAB(mM)


1.4814816
1.4814814
1.4814812
1.4814810
1.4814808
1.4814806
1.4814804
1.4814802
Γ×10^6 (mol/m^2)
(d)
0.0
0.1
0.2
0.3
0.4
0.5
Concentration of CTAB (mM)


1.0900474
1.0900473
1.0900472
1.0900471
1.0900470
Γ×10^6 (mol/m^2)
0.0
0.1
0.2
0.3
0.4
0.5
Concentration of CTAB (mM)
(e)


1.0975610
1.0975609
1.0975608
1.0975607
1.0975606
1.0975605
1.0975604
1.0975603
Γ×10^6 (mol/m^2)
0.0
0.1
0.2
0.3
0.4
0.5
Concentration of CTAB (mM)
(f)


1.020250
1.020245
1.020240
1.020235
1.020230
1.020225
1.020220
Γ×10^6 (mol/m^2)
0.0
0.1
0.2
0.3
0.4
0.5
(g)

A

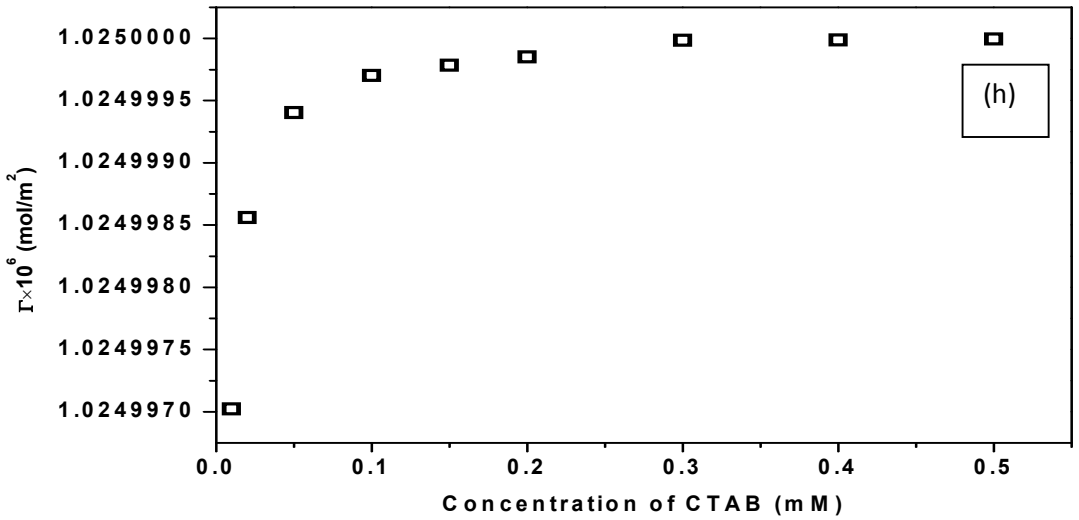


Figure 5.1 Adsorbed amount ┌ of CTAB plotted versus the concentration of CTAB as calculated with Langmuir model for **(a)** NaCl (0.05M), **(b)** NaCl (0.15M), **(c)** $CaCl_2$ (0.05M), **(d)** $CaCl_2$ (0.15M), **(e)** Na_3PO_4 (0.05M), **(f)** Na_3PO_4 (0.15M), **(g)** Na_2SO_4 (0.05M), **(h)** Na_2SO_4 (0.15M).

According to the surfactant adsorption values it is observed that the former values increases with increase in salt concentration. Similar behavior has also been reported for various hydrocarbon-water interfaces in presence of NaBr by Moradi et al. [24]. This behavior can be attributed to the fact that increase in concentration of salt attracts more molecule to adsorb at the interface in a faster manner to form the monolayer. But when it comes to compare the univalent and bivalent ions, the bivalent ions provides less electrostatic repulsion screening thereby decreasing the surfactant adsorption.

5.2.2 The Frumkin Adsorption Isotherm.

The Frumkin model considers the lateral interactions between the adsorbed molecules so it describes well the behaviour of surfactant molecules. We have used Frumkin Ionic Compressiblity model for ionic surfactants in salt aqueous solutions. The equation accounting for average activity of all ions present in solution is given by:

$$b[c(c+c_2)]^{1/2}f = \frac{}{1-}\exp(-2a)$$

Where c_2 is the additional salt concentration and f is the activity coefficient which can be obtained from the Debye-Huckel equation.

And the equation of state is given by:

$$\prod = -\frac{2RT}{\boldsymbol{\omega_0}} [\ln(1-) + a^2$$

Where ∏ is the surface pressure, b is the adsorption equilibrium constant, a is the Frumkin interaction constant, R and T are universal gas constant and temperature.

In the above equation it is assumed that the maximum molar area of adsorbed surfactant is equivalent to double molar area of solvent. Also the surface coverage ɵ is given by:

$$= \omega$$

Here it is assumed that the molar area, ω depends on surface pressure which is given as:

$$\omega = \omega_0(1 - \epsilon \prod)$$

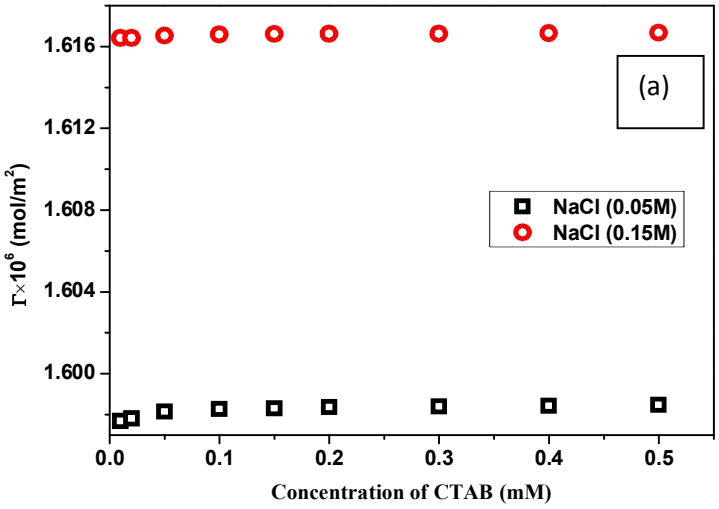
We have used the software Isofit for fitting the experimental interfacial tension data. Two different concentrations of 0.05 M and 0.15 M of each salt was used. The values of adsorption parameters is given in Table 5.3.

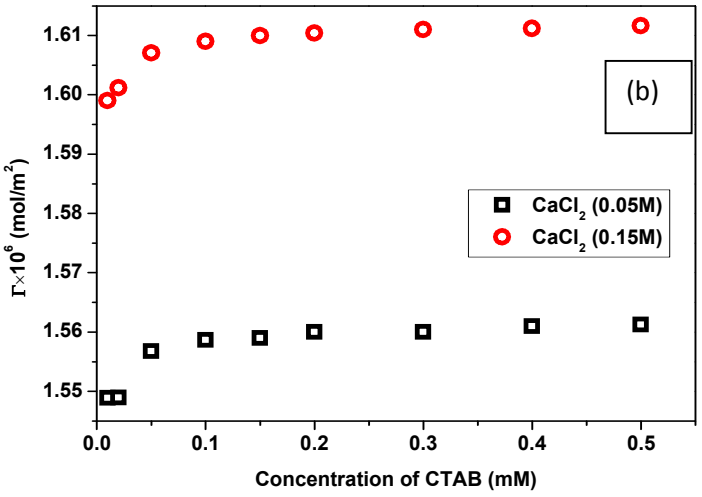
Table 5.3 Parameters of adsorption layer obtained with Frumkin model at sunflower oil water interface.

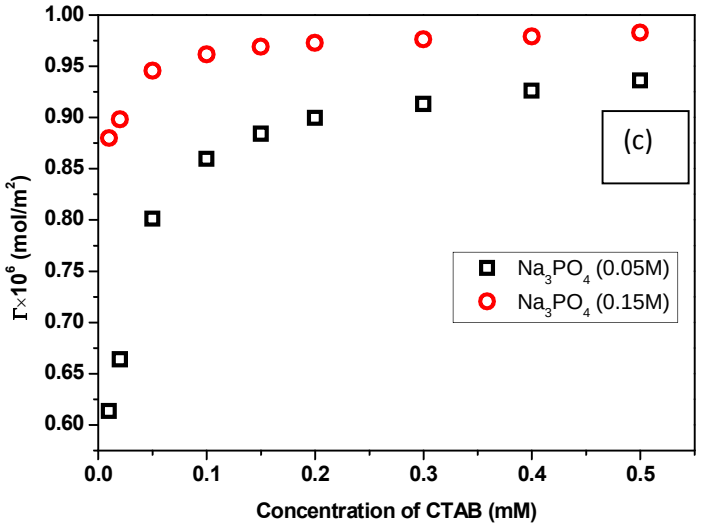
S.No.	**Electrolyte**	**Concenteration of electrolyte**	**€(%)**	**a**	**b(1/mmol)**	**ω(m^2/mol)**
1	NaCl	0.05 M	1.95	0.60	$3.73*10^7$	$6.20*10^5$
2	$CaCl_2$	0.05 M	1.47	0.60	$3.76*10^7$	$6.40*10^5$
3	Na_3PO_4	0.05 M	2.76	0.40	$1.09*10^6$	$1.0*10^6$
4	Na_2SO_4	0.05 M	2.80	0.46	$1*10^6$	$1.8*10^6$
5	NaCl	0.15 M	2.48	1.02	$3.02*10^8$	$7.6*10^5$
6	$CaCl_2$	0.15 M	2.51	1.02	$1.92*10^8$	$6.26*10^5$
7	Na_3PO_4	0.15 M	2.55	0.44	$1.94*10^6$	$1*10^6$
8	Na_2SO_4	0.15 M	2.68	0.48	$1.5*10^6$	$1.8*10^6$

From the table it is observed from '**€**' values that Frumkin model gives better fitting of experimental data which is due to the fact that Langmuir model is based on assumption of

absence of lateral interactions which is not valid for surfactant solutions. The parameter 'a' is an indicator of interactions which include inter- ion interaction and van der waals intreractions. In all cases positive values of 'a' are obtained which shows attractive nature of forces for surfactant molecules at interface. The values of 'a' increases with concentration of electrolyte which shows that higher concentration of electrolyte leads to more attraction for surfactant molecules at interface. Also the value of adsorption constant i.e. 'b' is highest for 0.15 M NaCl leading to more adsorption of CTAB at interface.







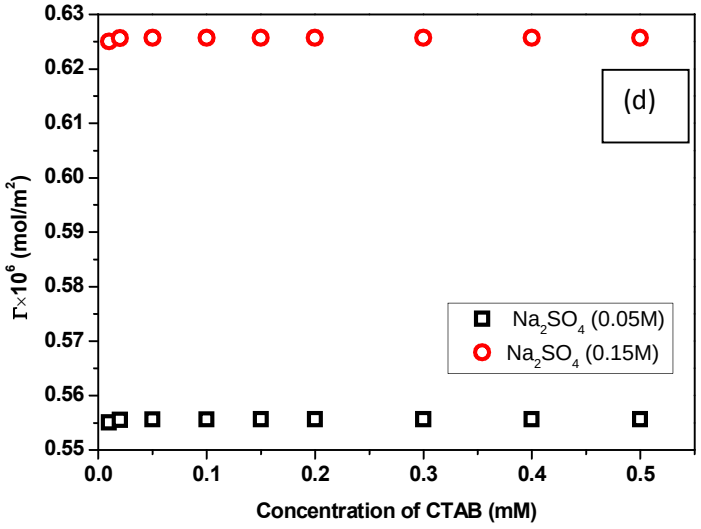


Figure 5.2 Adsorbed amount ┌ of CTAB plotted versus the concentration as calculated with Frumkin model for **(a)** NaCl (0.05M and 0.15M), **(b)** $CaCl_2$ (0.05M and 0.15M), **(c)** Na_3PO_4 (0.05M and 0.15M), **(d)** Na_2SO_4 (0.05M and 0.15M).

The surfactant adsorption calculated by fitting experimental interfacial tension data with Frumkin model is shown in Figure 5.2. From the figures it can be interpreted clearly that adsorption of surfactant increases with concentration of surfactant as well as electrolyte but near to CMC values, surface saturation is seen. The surfactant molecules can be imagined to orient with the hydrophobic group close to the surface and hydrophilic group oriented towards aqueous

phase. The continuous adsorption process will make the molecules oriented in a regular fashion. When electrolyte is added, the repulsion between the surfactant headgroups is decreased which increases the potency of adsorption. In all the cases of electrolytes adsorption is enhanced by ionic strength. Addition of electrolyte increases the number of surfactant ions in stern layer for maintaining the electrical neutrality. There is quite a difference in ability of various anions to facilitate the adsorption of cationic surfactant. On comparing NaCl, Na_2SO_4 and Na_3PO_4, it is observed that NaCl leads to more surfactant adsorption. Also for the same anion chloride, the cation sodium gives more adsorption when compared to calcium ion which is due to less repulsions with sodium ion the packing of surfactant molecules becomes more compact.

CHAPTER 6

CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

Conclusions.

The results presented in Chapter 4 and 5 on the effect of electrolyte on interfacial tension and adsorption of surfactant at sunflower oil water interface can be summarized as follows.

The addition of surface active additives in water modify the surface phenomena which is further influenced by addition of electrolytes. Equilibrium interfacial tension values were measured using Du nuoy ring tensiometry technique to examine the interfacial tension characteristics of surfactants in presence of electrolytes. Addition of 0.15 M NaCl gives lowest interfacial tension and highest surfactant adsorption. In case of calcium chloride and sodium chloride interfacial tension decreases at concentrations only below CMC of pure surfactant after which it starts increasing which suggest the penetration of cations in surfactant layer at higher conncentrations due to latent coagulation which ultimately will lead to repulsion. However for sodium phosphate and sodium sulphate the interfacial tension decreases upto concentrations even above CMC of surfactant solution. This may be due to the alkaline nature of phosphate and sulphate ions. The trend shown by the electrolytes for dilute electrolyte solutions is in agreement with the Hofmeister series.

The theoretical curve fits were made to experimental data using Frumkin and Langmuir models to compare the effect of different electrolytes. The resulting parameters obtained showed that Frumkin model fits better to the experimental data. Sodium chloride increases the tendency of CTAB to adsorb at the surface the most. The conclusion drawn by comparing the adsorption parameters agreed well with the adsorption of surfactant.

SUGGESTIONS FOR FUTURE WORK

This work can be further channelized in different avenues, namely-

(1) The work conducted has been done using cationic surfactant, similar study can be done using natural surfactants.

(2) The work has been carried out using sunflower oil. Similar studies can be done using different vegetable oils which are used in cosmetics and co-relate between the obtained results.

(3) The effect of nanoparticle can be carried out.

(4) Rheology study of same system can also be carried out.

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